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13. ABSTRACT ***(Maximum 200 Words)***

This Summary Report describes the results of more than two years of research conducted with funding provided by SERDP, the Marine Corps Logistic Bases (MCLB) and the Navy Department's LINC (Repair Technology) Program. The research focused on the destruction of VOCs in paint booth exhaust using hybrid air pollution control technologies. The hybrid system selected included three principle modules: UV photochemical destruction; counter-flow packed bed scrubbing using activated oxygen; and granular activation of carbon adsorption with subsequent oxidative regeneration of the carbon. The stated goals of the research included enhanced understanding of this set of technologies to support design of smaller, more affordable treatment system for both DoD and commercial application. The research was unique in that baseline data was collected on a pilot scale system concurrent to the more traditional modeling and bench scale experimentation. This approach provided confirmation of bench scale results well within the funded period of research.

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STRATEGIC ENVIRONMENTAL RESEARCH AND DEVELOPMENT PROGRAM AIR TREATMENT PROJECT: FINAL SUMMARY REPORT AND BIBLIOGRAPHY

J. M. Schneider

Technical Memorandum
File No. 96-026
15 March 1996

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Covering the period from October 1, 1993 to September 30, 1995

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EXECUTIVE SUMMARY

This Summary Report describes the results of more than two years of research conducted with funding provided by the Strategic Environmental Research and Development Program (SERDP), the Marine Corps Logistics Bases (MCLB) and the Navy Department's LINC (Repair Technology) Program. The research focused on the destruction of VOCs (Volatile Organic Compounds) in paint booth exhaust using hybrid air pollution control system technologies. The hybrid system selected included three principle modules: UV photochemical destruction; counter-flow packed bed scrubbing using activated oxygen; and granular activated carbon adsorption with subsequent oxidative regeneration of the carbon. The stated goals of the research included enhanced understanding of this set of technologies to support design of smaller, more affordable treatment system for both DoD and commercial application. The research was unique in that baseline data was collected on a pilot scale (2500 cfm) system concurrent to the more traditional modeling and bench scale experimentation. This approach provided confirmation of bench scale results well within the funded period of research.

The research showed that hybrid systems clearly have a role in the treatment of exhaust streams typical of those found in manned paint booth applications. The body of knowledge on the use of granular activated carbon in this and similar applications, was substantially enhanced by this research as was the understanding of counterflow water scrub and UV photolysis. Several conclusions should have immediate effect on systems being designed now, and the knowledge and models described here-in should enhance systems for years to come.

A program to formulate a new lower VOC generation of chemical agent resistant coatings (CARC) was initiated by the MCLB concurrent to the final months of this research. Treatability studies were conducted on the new CARC's solvents during the final phases of the formulation process, providing assurance to the MCLB and other potential users that the treatment technologies are a good match with the new CARC.

A full scale 45,000 cfm hybrid system has been installed at MCLB, Barstow, CA and is now operational. This offers the opportunity to perform additional testing on a full scale system to validate pilot scale and bench scale findings. It also offers the potential to examine the dynamics of a continuously operating system over its first year of use.

The obvious benefits of such concurrent testing and the promise shown by the set of hybrid technologies suggest that continued R&D funding should be provided for this project.

ABSTRACT

The Strategic Environmental Research and Development Program (SERDP) has funded the Environmental Programs Group at The Applied Research Laboratory (ARL) to perform bench scale and pilot scale research on a hybrid air treatment technology commercially available from Terr-Aqua Enviro Systems, Inc. The Marine Corps Multi-Commodity Maintenance Centers $(MC)^3$, spurred by their need to reduce volatile organic compound (VOC) emissions from facility paint spray booths, sponsored the research at ARL and had oversight of the project. A research agreement was formed between ARL and Terr-Aqua Enviro Systems, Inc. (TAES) to facilitate rapid technology transfer of significant finding to the commercial sector.

During the two year project, a significant amount of research was undertaken in ultraviolet photochemical degradation of VOCs, in counter flow packed bed scrubbing of VOCs from the air and subsequent activated oxygen degradation, and in granulated activated carbon adsorption of VOCs with subsequent oxidative regeneration of the carbon.

This research has provided much insight into the overall operation of the TAES hybrid system and into each of its component technologies. It was determined, for example, that the pilot scale system resulted in a 95% reduction in air stream VOCs; that the adsorption capacity of the carbon decreases over time, but that it still retains considerable loading capacity even after as many as eight years of use; that N-methyl-2-pyrrolidinone (NMP), a constituent in the latest generation of chemical agent resistant coatings (CARC), is readily removed from the air stream by the aqua reactors; that degradation of NMP is enhanced by the addition of hydrogen peroxide and increased pH. The research also suggests that biodegradation might play a major role in the degradation achieved in the carbon bed.

In addition to these general findings, the research suggests several system modifications that would result in increased efficiency or reduced capital costs. *Increased removal and/or destruction efficiency* of the system might be achieved by modification of the photolytic reactors to increase residence time and light intensity, and by modification of the carbon bed to allow better contact between carbon and ozone. The addition of hydrogen peroxide and/or increasing the pH of the water phase is a low cost modification expected to increase the degradation of many organic compounds absorbed into the water phase. *Reduced capital investment* in future systems would be achieved with no loss in efficiency, by the elimination of the mist air dispersion units, and by customer specific modifications for treating air streams high in chlorinated hydrocarbons.

In addition to the obvious value of the research findings noted herein, an excellent, unique, state-of-the-art research facility has been established. This facility and the findings thus far should provide a springboard for future work in air and water treatment, particularly the oxidative reduction of VOCs.

These findings are significant and point to many different areas for further research with extensive possibilities for system optimization, enhancement, and cost reduction. No testing was performed on the full scale system at Barstow since funding expired prior to its start-up. Additional funding sources are being sought to continue this work.

Detailed quarterly reports of technical progress have been provided to the Marine Corps, the Mojave Desert Air Quality Management District, Terr-Aqua, and members of the SERDP program throughout the project. This report summarizes the project and the various studies undertaken. In addition it provides an annotated bibliography of the numerous publications which have resulted from the work.

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1.0 INTRODUCTION

1.1. Statement of Problem/Background

The Marine Corps Logistics Bases (MCLB) operates two maintenance centers, one in Albany, GA, and one in Barstow, CA, referred to as the Marine Corps Multi-Commodity Maintenance Centers $(MC)^3$. At these centers, Marine Corps vehicles are serviced, repaired and maintained. This process generally includes painting and vapor degreasing operations which generate low levels of airborne volatile organic compounds (VOCs) and hazardous air pollutants (HAPs), which are then exhausted to the atmosphere. Increasing Federal regulations, particularly the Clean Air Act Amendments of 1990, and state regulations, especially in California, require that these emissions be reduced and controlled.

One goal of the Marine Corps Multi-Commodity Maintenance Centers is to be compliant with all local, state, and federal emissions regulations and, in particular, to demonstrate continuous reductions in VOC and HAP emissions. In 1992, the Letterkenny Army Depot and ARL Penn State surveyed and reviewed commercially available air treatment technologies. Technological advantages and disadvantages were reviewed as they applied to treatment of paint booth exhaust air streams. A detailed cost analysis was done as well. This analysis concluded that, among the available technologies, UV-oxidation systems were the most cost effective.[1] Based on this report, MCLB selected a UV-oxidation system for installation at their Barstow facility.

In early 1993, MCLB submitted a joint proposal with the U.S. Environmental Protection Agency (USEPA) to the Strategic Environmental Research and Development Program (SERDP) with the goal "to achieve rapid improvement in the quality of air emissions from paint spray booths and vapor degreasing tanks at $(MC)^3$ Barstow and $(MC)^3$ Albany and develop information on advanced air pollution prevention and control approaches."[2]

The team for the overall SERDP project included the U.S. Marine Corps Logistics Bases (MCLB) and the U.S. Environmental Protection Agency (USEPA) Air and Energy Engineering Research Laboratory (AEERL). The air treatment segment of the project, which is the subject of in this report, was accomplished by the Marine Corps Logistics Bases. Technical and research support was provided to MCLB by the Applied Research Laboratory at The Pennsylvania State University (ARL Penn State). In addition, a cooperative agreement was signed between ARL Penn State and Terr-Aqua Enviro Systems, Inc. to allow rapid transfer of research findings to the marketplace.

ARL Penn State's responsibility was to perform laboratory research and experimentation to achieve the following technical objectives, as outlined in the SERDP project proposal:

- Enhance the understanding of the use of coherent energy sources which initiate radical oxidation processes to destroy VOCs.
- Enhance the understanding of the emissions reduction potential of TAES and other enhanced VOC destruction technologies.
- Apply lessons learned in modeling and experimentation to the design of optimal VOC control system configurations.[2]

This "enhanced understanding" would lead to system improvements which would result in size and/or cost reductions of future air treatment systems purchased by (MC)[3] and other DoD or industrial sites.

The proposal was accepted and funded by SERDP for two years, beginning October 1993, and ending September 30, 1995.

1.2. Funding

This project was funded in large part by SERDP, but also by several other organizations, by providing either direct or indirect funding, or by providing equipment for use in the project.

Of the total SERDP funding provided for this project, $1.38 million was directed to ARL Penn State over two years for this research. The Marine Corps provided $87,000 to develop a specification for the full scale Barstow air treatment system and to initiate the early phases of the research. Additionally, the MCLB invested $2.2 million in the full scale APCS. The Navy's LINC/REPTECH program provided additional financial support to ARL Penn State for this project during the two years that SERDP was funding the project. In addition, since SERDP funding expired September 30, 1995, LINC/REPTECH has continued as the sole source of funding for continuing and wrap-up studies. At completion, it is estimated that LINC/REPTECH will have provided about $200,000 in support of this work.

Terr-Aqua Enviro Systems, Inc., provided the pilot scale air treatment system to The Pennsylvania State University. Graseby Nutech donated analytical instrumentation, and Fisher-Rosemount loaned additional instrumentation for use in this project. Without these gracious gifts, this program could not have been executed.

Two graduate students, Meryl R. Mallery and Paul D. Paulsen, were funded in part by GAANN Fellowships, sponsored by the US Department of Education and Penn State to emphasize environmental academics and research. Jay S. Dusenbury was funded in part by an Augmentation Award for Science and Engineering Research Training (AASERT), sponsored by the Department of Defense. Several undergraduate students were funded through a special ARL Penn State ROTC program and by minority student research opportunity programs, and three undergraduate students worked for credit only. Four of these undergraduate students performed small research projects of their own, while the remainder provided general laboratory assistance and data collection for bench scale and pilot scale studies.

1.3. Approach

Under the SERDP proposal, ARL Penn State was to perform laboratory research and experimentation to enhance the understanding of the TAES technologies, and to apply the lessons learned to the design of optimal VOC control system configurations.[2] In order to reach these goals, ARL Penn State performed modeling and bench scale experimentation on each of the three basic technologies included in the Terr-Aqua Enviro System, Inc. air pollution control system (APCS), while at the same time collecting baseline data on a pilot scale system. As results and significant findings of bench scale research became available, these were to be scaled-up to the pilot scale system; pilot scale runs using promising modifications would be compared to the baseline data. Once "proven" or demonstrated on the pilot scale system, the modifications could be readily transferred via a research agreement to Terr-Aqua for incorporation into future systems. This iterative approach of bench scale research, pilot scale validation, scale-up to commercial, followed by further research would result in quick release of system improvements to the marketplace and a continually improving technology. A schematic of this approach is presented in Figure 1.

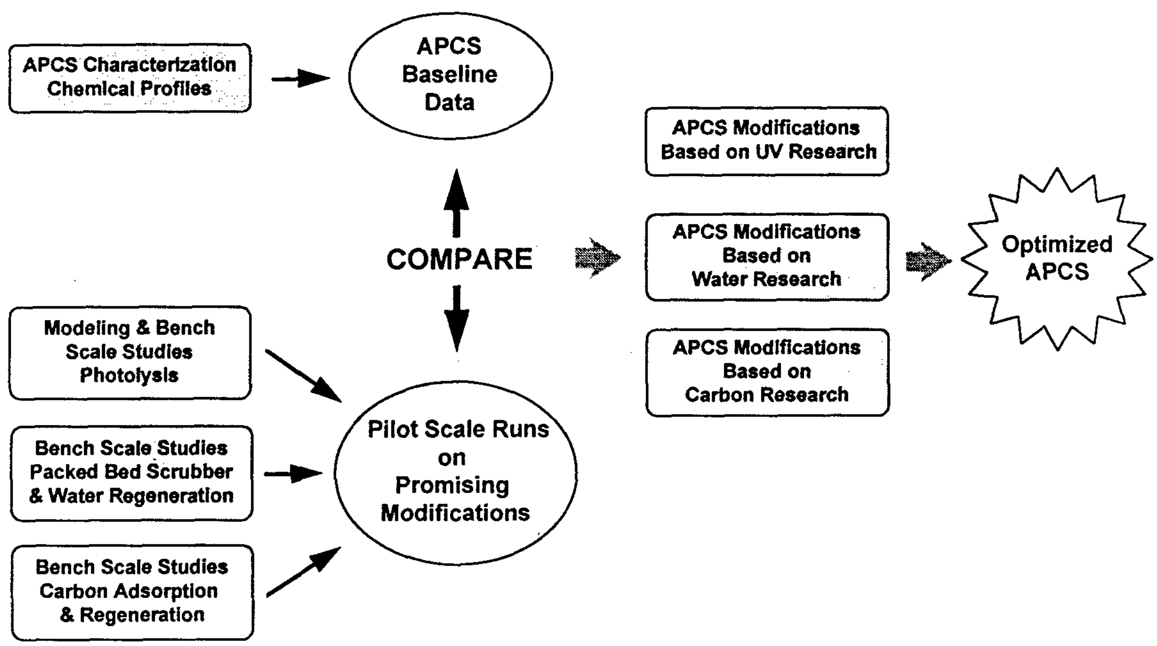

Figure 1. SERDP research plan

Research performed at ARL Penn State under this proposal included the following areas of focus:

- bench scale research and modeling of the photolytic reactor and photolytic degradation processes,
- bench scale research on the packed bed scrubbers and oxidative regeneration of the water,
- bench scale research on granulated activated carbon adsorption and oxidative regeneration, and
- baseline studies on the pilot scale air treatment system.

Within the time frame of the funding, studies to scale-up and validate the research findings, and testing of the full scale system could not be performed. Alternate sources of funding are being sought to continue this research.

2.0 EXECUTION

2.1. Organization

Mr. Ron Vargo and Mr. John House of MCLB, Albany, GA were the Marine Corps' technical and contracts managers, respectively.

Lewis C. Watt, Manager of Environmental Programs, was project director at ARL Penn State. Dr. Robert J. Heinsohn, Professor of Mechanical Engineering and Dr. Fred S. Cannon, Assistant Professor of Civil Engineering were co-principal investigators for the project.

Pilot scale studies were designed and coordinated by Janice M. Schneider, Research Assistant at ARL; assistance in analytical methods development and validation was provided by Ms. Schneider as well. Bench scale research was performed by graduate students in Environmental Engineering and Environmental Pollution Control. Additional research and much assistance was provided by numerous undergraduate engineering students.

A complete listing of personnel involved in this project is provided in Table 1.

Table 1
PERSONNEL INVOLVED IN SERDP PROJECT

NAME	AFFILIATION	ROLE
Ron Vargo	Marine Corps	Technical Manager
John House	Marine Corps	Contracts Manager
Lewis C. Watt	Applied Research Lab	Project Director
Robert J. Heinsohn	Penn State, ME	Co-Principal Investigator
Fred S. Cannon	Penn State, CE	Co-Principal Investigator
John Cimbala	Penn State, ME	Professor, Research Advisor
Janice M. Schneider	Applied Research Lab	Analytical Chemist, Project Coordinator
Leslie Johnson	Applied Research Lab	Facilities Coordinator,.Spray Booth
Timothy A. Spaeder	ARL/PSU, M.S., PhD.	Photolytic Research
Bradley A. Striebig	ARL/PSU, PhD.	Water Treatment Research
Jay S. Dusenbury	ARL/PSU, PhD.	Carbon Research
Meryl R. Mallery	ARL/PSU, M.S.	Photolytic Modeling
Jyoti Singh	ARL/PSU, M.S.	Carbon Research
Meghan Pace	ARL/PSU, M.S.	APCS Baseline Studies
Paul D. Paulsen	ARL/PSU, PhD.	Carbon Research
Brian Moore	ARL/PSU, M.S.	Carbon Research
Chariti Young	ARL/PSU, B.S.	Photolytic Modeling
Dave Mazyck	ARL/PSU, B.S.	Carbon Research
Dave Maurer	ARL/PSU, B.S.	Carbon Research
Ron Rabickow	Penn State, B.S.	Spray Booth Model
Mark Hazenberg	ARL/PSU, B.S., ROTC	General Lab Assistance
John Brabazon	ARL/PSU, B.S., ROTC	General Lab Assistance
Steve Johnson	ARL/PSU, B.S., ROTC	General Lab Assistance
Rob Heffner	ARL/PSU, B.S., ROTC	General Lab Assistance
Lisa Albricht	Penn State, B.S.	General Lab Assistance

2.2. Research Agreement

A cooperative research agreement was established between ARL Penn State and Terr-Aqua Enviro Systems, Inc. This alliance allows for rapid transfer of promising system modifications to new TAES systems under construction, significantly reducing the delay typically encountered in scale-up of bench scale research to commercial systems.[3]

2.3. Facilities and Equipment

2.3.1 Laboratory

A 1600 square foot laboratory was established in Research Building West at ARL Penn State. The laboratory houses the pilot scale air treatment system described in Section 2.3.2, and bench scale apparatus and analytical instrumentation primarily related to the photolytic reactors and the packed bed scrubbers. Additional facilities were established within the Civil Engineering department, primarily for bench scale research related to the granulated activated carbon (GAC).

State-of-the-art analytical instrumentation was purchased for use in the project. This includes several gas chromatographs with a variety of detectors, including a mass selective detector (mass spec) for identification of organic intermediates and breakdown products, cryogenic sample concentrators for analysis of low level organics in air, and thermogravimetric analyzers for highly sensitive carbon analysis. A complete listing of the analytical instrumentation and related laboratory equipment used for this project is presented in Table 2.

2.3.2 Pilot Scale Air Treatment System

A pilot scale, 2500 scfm air pollution control system (APCS) was constructed at ARL Penn State for use in these studies. The system, which was designed and installed by Terr-Aqua Enviro Systems, Inc., parallels their commercially available units in scale and in design of system components. It differs from commercially available units in size, of course, and in several ways that allow the unit to be more flexible for research purposes. In addition, the two pilot scale system carbon adsorption units are in series, rather than in parallel as they are in commercial scale systems.

This treatment system uses a self-contained, self-regenerative multistage process that does not rely on incineration and produces no waste stream of its own. A schematic diagram of the pilot system is shown in Figure 2.

Table 2
LABORATORY EQUIPMENT AND INSTRUMENTATION

- Hewlett Packard 5890 Series II gas chromatographs (two) with Flame Ionization, Thermal Conductivity and Electron Capture Detectors
- Hewlett Packard 5890 Series IIG gas chromatograph fitted with Hewlett Packard 5972 Mass Selective Detector
- Graseby Nutech 8533 Universal Automatic Sample Concentrator with cryoconcentrator and cryofocusing system
- Graseby Nutech 3550 Sample Concentrator
- Graseby Nutech Model 2800 VOST sampling system, and Graseby Nutech Model 8513 VOST cartridge conditioning system
- Kin-Tek Laboratories Model 491M Gas Standards Generator
- Dasibi 1008-HC UV Photometeric ozone meter
- Optronics Laboratories 730C Programmable Radiometer/Photometer
- Terr-Aqua Vacuum Ultraviolet Photochemical ozone generators
- Fisher-Rosemount NGA 2000 Series Gas Analyzer with FID
- Cahn 120 and 121 Thermogravimetric Analyzers
- Barnat Company model 47503010 Pump
- Tedlar bags from SKC, Inc.
- Solvents from Aldrich Chemical Company, Inc.
- VOCOL Capillary Columns from Supelco, Inc.
- Solid Phase Microextraction Fibers from Supelco, Inc.

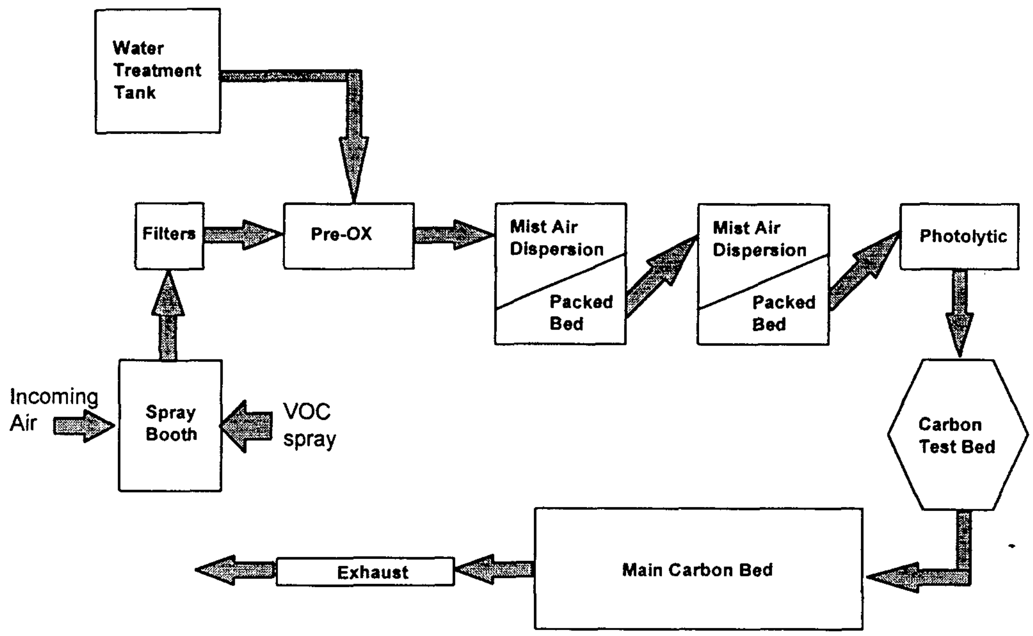

Figure 2. Schematic of 2500 cfm Terr Aqua pilot scale air treatment system.

The system contains three independent units, each based on a unique VOC removal concept:

- a gas-phase photolytic reactor which uses UV radiation and ozone to initiate photolytic, photocatalytic and free radical reactions to oxidize VOCs,
- an aqua reactor which uses a counter-flow packed bed scrubber, a mist air dispersion unit, and an ozonating water treatment tank to absorb and oxidize VOCs, and
- a granular activated charcoal (GAC) unit which absorbs VOCs.

Both the water and the GAC are regenerated within the pilot unit using ozone.

A spray booth was designed and built as an inlet to the air treatment system. This spray booth utilized a commercially available paint spray gun to allow spraying of organic solvents into the incoming air stream to essentially contaminate the air to known levels before treatment in the system.

3.0 RESEARCH

3.1. Bench Scale Research

3.1.1 Photolytic Reactors

Bench scale research, computer modeling and physical modeling of the photolytic reactors were performed under the direction of Dr. Robert J. Heinsohn, Professor of Mechanical Engineering at The Pennsylvania State University.

A computer model of the photolytic reactor was developed by M. Mallery. This model incorporates a light intensity distribution model, a velocity field model, and the chemical kinetics of formaldehyde and methanol photochemical destruction into a single numerical model. Using this model, concentrations and flow rates of various reactants can be varied and the effects visualized in colorized 2-dimensional concentration grids. The model demonstrated that $OH^{\bullet}$ radicals, formed by the ultraviolet (uv) light and the key initiator of photolytic degradation, are present only in the immediate vicinity of the light bulb. This means that, for $OH^{\bullet}$ initiated photolytic degradation to occur, the VOCs in the air stream must come into close contact with the bulb. This model has also shown that the degradation of photolytically active VOCs is enhanced by increased residence time, increased humidity, optimized light intensity, and proper wavelength selection. Further investigation of these variables and a modified photolytic reactor, possible including bulbs of more than one wavelength, could greatly increase the degradation seen in this component.

Ms. Mallery's model could be modified by including the chemical kinetics reactions (if available) for additional organic compounds. However, the most significant findings of her model were related to the production of $OH^{\bullet}$ radicals by the ultraviolet lights. These findings are unrelated to the organic compounds being treated; increased production of $OH^{\bullet}$ radicals would result in increased degradation of any photolytically active compounds.

A physical, flow-visualization model of the photolytic reactor was built by C. Young using the same physical configuration as used in the computer model above. By heating oil to create streams of smoke and then taking photographs as the smoke passed over the uv bulbs, the physical model was used to visualize and verify the computer model.

A bench scale photolytic reactor was designed and built by T. Spaeder (Figure 3). This reactor was used to investigate the effects of ozone concentration, methanol concentration, and uv photolysis on the degradation of air stream methanol. Initial results confirm the findings of M. Mallery's computer model; at the time of this writing, further data analysis is underway.

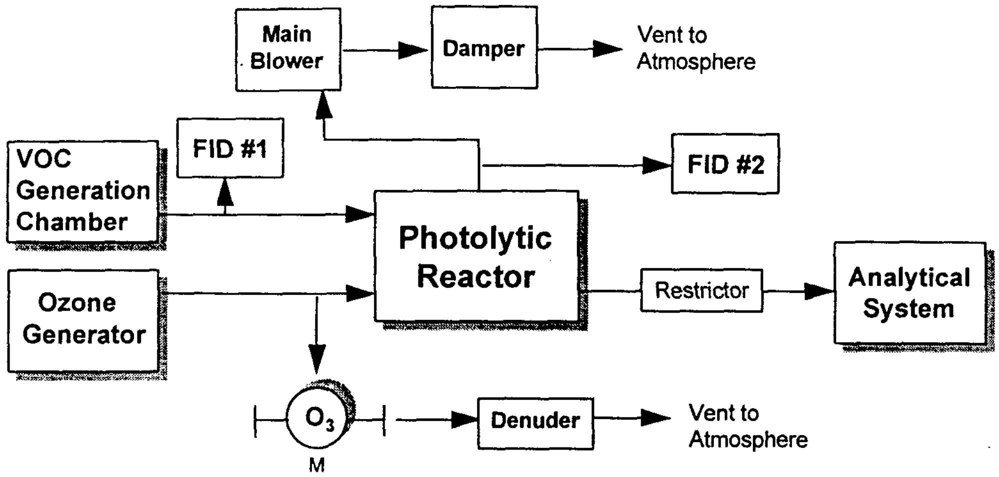

Figure 3. Schematic of the bench scale photolytic reactor.

Results of these three studies and related work are summarized in the abstracts in Appendix A; details of the work can be found in the references cited.

3.1.2. Packed Bed Scrubbers

A bench scale packed bed scrubber and a bench scale water treatment tank (Figure 4) were designed and built by B. Striebig. These reactors were used to study the removal of N-methyl-2-pyrrolidinone (NMP) by the packed bed scrubber and its subsequent degradation in ozone and hydrogen peroxide enriched solutions. NMP is a primary constituent in the latest generation of chemical agent resistant coating (CARC) paint. Mr. Striebig found that NMP is easily removed from the air stream in the packed bed scrubber, and that its degradation is enhanced by the addition of hydrogen peroxide and increasing the pH to 9.

According to the literature, the addition of hydrogen peroxide and/or increasing the pH changes selective molecular *ozone* reactions to non-selective (and rapid) *hydroxyl radical* reactions.[4] This increased production of hydroxyl radicals results in increased degradation of many organic compounds.[4]

This research was performed under the direction of Dr. Robert J. Heinsohn, Professor of Mechanical Engineering at The Pennsylvania State University. Results are summarized in the abstracts in Appendix B; details of the work can be found in the references cited.

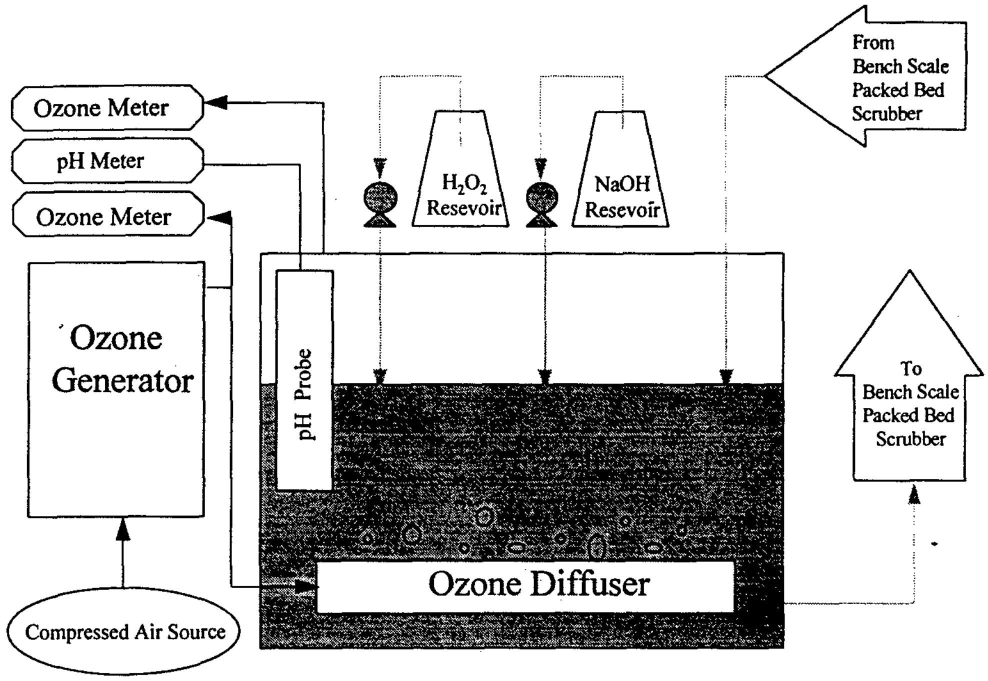

Figure 4. Schematic of bench scale water reactor.

3.1.3 Granulated Activated Carbon

Bench scale research on the physical characteristics, adsorption mechanisms, and regeneration of granulated activated carbon were performed under the direction of Dr. Fred S. Cannon, Assistant Professor of Civil Engineering at The Pennsylvania State University.

J. Singh obtained samples of granulated activated carbon which had been exposed for various lengths of time to the daily loading and ozonation cycles in commercial TAES units. Ms. Singh then studied the changes in pore volume, surface area, surface oxygen content, and VOC adsorption capacity for these samples relative to their age and exposure. Her findings showed that over hundreds of cycles of loading and regeneration, adsorption capacity of the carbon decreases. This is more notable for polar than for non-polar compounds, and more significant when higher molecular weight compounds were being loaded. However, even after several years of loading and regeneration, the carbon still retained "considerable" loading capacity (35-95%, depending on the compounds involved), and was infinitely more useful than thermally regenerated carbon of the same age.

Initial studies by Mr. Dusenbury in a bench scale carbon bed reactor (Figure 5) have shown that much of the ozone penetrates the carbon to a depth of one to two inches. Only a slight fraction penetrates deeper. Thus in a 10-12 inch bed, much of the carbon is being exposed to only a slight fraction of the ozone. Increased activity in the carbon bed might result from a modified geometry which allows closer contact between the ozone and the carbon at more frequent intervals throughout the depth of the bed. Possible geometry modifications include a series of thinner carbon beds, or the addition of ozone at locations throughout the depth of the bed, instead of just at the surface.

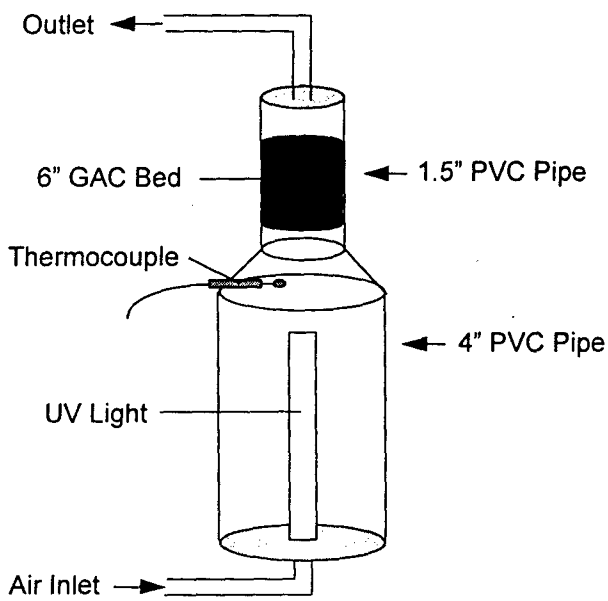

Figure 5. Schematic of bench scale carbon bed apparatus.

Mr. Dusenbury also collected samples of carbon from a used, commercial scale Terr-Aqua system, and Mr. Moore performed solvent extractions of the samples. The carbon was found to be covered with a white, filamentous material and showed biological growth. This biological growth was inoculated into laboratory scale GAC columns and preliminary results suggest that this biological growth reduces VOC concentrations considerable. These findings are very preliminary but indicate that [in the continuously moist, oxygenated environment of the carbon bed, with organic matter (VOCs) continuously flowing past], biodegradation may play a major role in the degradation of VOCs in the carbon bed. Mr. Dusenbury's biodegradation studies are continuing under funding provided by AASERT; expected completion date is May, 1997.

Answers to the questions raised by Mr. Dusenbury's research are key to understanding the functioning of the Terr-Aqua system. Additional studies should be conducted concurrently on the full scale system at Barstow.

Mr. Moore's extraction analysis of the above carbon samples revealed that the GAC had adsorbed VOCs throughout its bed depth, with slightly higher loading at the front of the bed than at the back.

Mr. Paulsen is using a Thermogravimetric Analyzer (TGA), which is an extremely sensitive analytical balance, to measure the VOCs adsorbed and desorbed by single grains of carbon. His research seeks to characterize the way that VOCs are loaded onto individual carbon grains, and how these carbon grains can be regenerated for reuse. Mr. Paulsen's research will develop a fundamental understanding of how VOCs diffuse through the pores of the GAC, how the affinity of the VOCs for the carbon surface affects regeneration, and how temperature and ozonation alter this affinity. Along with his laboratory findings, he is developing a numerical model to describe his findings and to predict further findings.

Results of these studies and related work are summarized in the abstracts in Appendix C; details of the work can be found in the references cited.

3.2. Pilot Scale Studies

Pilot scale studies were performed by J. Schneider with assistance from M. Pace, B. Striebig, M. Mallery and other students involved in this project.

The Material Safety Data Sheets (MSDS) for Chemical Agent Resistant Coatings (CARC) used by the Marine Corps were reviewed (Appendix E). Two reports detailing actual air emissions from $(MC)^3$ Barstow paint booths were also reviewed.[5,6] These reviews identified compounds from several classes of chemical compounds:

Table 3
CHEMICAL CLASSES FOUND IN PAINT BOOTH EMISSIONS

Chemical Class	Compounds in CARC or typical emissions
Ketones	methylethyl ketone, methylisoamyl ketone, methylisobutyl ketone
Alcohols	n-butyl alcohol
Acetates	hexyl acetate, butyl acetate, 2-ethoxyethyl acetate
Aromatic hydrocarbons	toluene, ethylbenzene, xylene

Based on this review, one solvent representative of each chemical class was selected to be sprayed into the pilot scale system. The solvents selected were methylethyl ketone (MEK), ethanol, ethylbenzene, and butyl acetate. In addition, trichloroethylene (TCE) was selected as representative of the chlorinated hydrocarbons typically used in degreasing operations. (Butyl acetate has not yet been run in the pilot scale system).

A standard set of pilot scale operating conditions was selected and each of the selected solvents was sprayed into the system. Both air and water samples were collected; ten air sampling ports (100m, 102, 104, 105, 106, 107 in, 107 out, 108 in, 108 out, and WTT) and six water sampling ports (W-A through W-F) are indicated on Figure 6. This allowed sampling of the air stream before and after each component of the system, and sampling of the water throughout the system. Air samples were tested by either a modified EPA Method 25A or a modified T0-14, and water samples were tested by gas chromatography as well. The data was plotted and analyzed to provide a baseline description of how the system removes and/or degrades a variety of volatile organic compounds, polar, non-polar, and chlorinated.

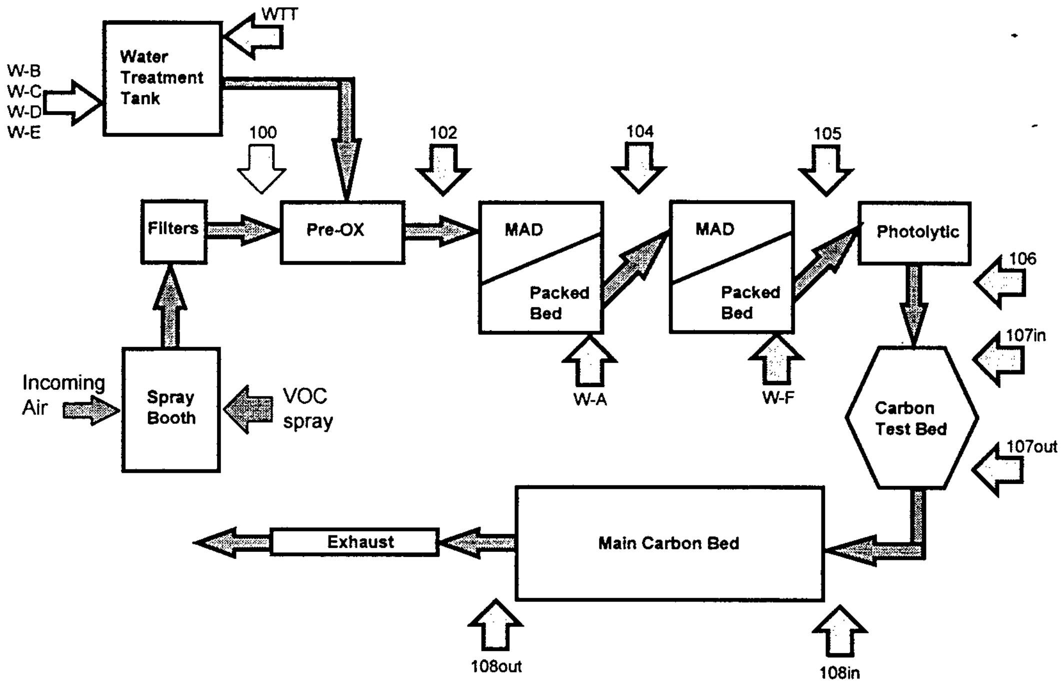

Figure 6. Schematic of 2500 cfm Terr Aqua pilot scale air treatment system with its ten air and six water sampling ports.

In a new system, and for the VOCs tested, the pilot scale system removed better than 95% of the VOCs in the incoming air stream. It was found that each of the VOCs sprayed into the system behaved differently, depending on its unique chemical and physical characteristics. For example, polar compounds like ethanol and MEK were mostly removed by the aqua reactors, while non-polar compounds like ethylbenzene were mostly removed by the carbon bed. The chlorinated compound, TCE, was largely degraded by the photolytic reactors. Each compound showed a distinctly different profile of absorption and degradation as the air stream passed through the system. Thus without any adjustment or modification to the existing Terr-Aqua technology, the hybrid system is very flexible and able to treat an air stream containing a wide array of solvent components.

Two experiments indicated that the mist air dispersion units did not increase the efficiency of the packed bed scrubbers. The amount of VOC removed (or destroyed) by the packed bed scrubbers alone was the same as that removed when the packed bed scrubbers and the mist air dispersion units were operated together. Additional studies should be done to verify these findings; removal of the mist air dispersion units from the TAES would result in a significant cost reduction.

It was also determined that as the water absorbed VOCs from the incoming air stream, it became "saturated" with the particular VOC, to the point where less and less VOC was removed from the air. This happened very quickly for non-polar VOCs, and over a longer period of time for polar VOCs. Because of this, it is imperative that the water treatment system be very efficient at destroying the VOCs in the water phase; if it is not, then VOCs will not be removed in the packed bed scrubbers. Efficiency of the packed bed scrubbers would be enhanced by rapid destruction of VOCs in the water treatment tank.

When trichloroethylene was sprayed into the system, it degraded rapidly in the photolytic reactors to hydrochloric acid, causing a rapid drop in pH of the water, and also after time, resulting in pitting of the stainless steel and corrosion of the carbon bed screens. System modifications such as pH control and elimination of the second photolytic reactor should be considered when treating air streams with high concentrations of chlorinated hydrocarbons.

Results of these studies are summarized in the abstracts in Appendix D; details of the work can be found in the references cited.

4.0 CONCLUSIONS AND RECOMMENDATIONS

In commercial use, the Terr-Aqua air treatment system has been reported by the manufacturer to remove over 95% of the VOCs found in incoming air streams, but the mechanisms and chemistry that cause this to happen were not well understood. The research undertaken by ARL Penn State in this SERDP project has provided significant knowledge about these mechanisms and has also suggested modifications that would improve system efficiency and/or reduce system cost.

While the reader is referred to the original papers for details of the research and detailed conclusions and recommendations, a number of general conclusions have been reached and are listed below. These conclusions are based on the research identified in this report, encompassing two years of bench scale studies and testing on a pilot scale hybrid air treatment system.

- The Terr-Aqua air treatment system, with virgin granulated activated carbon, removes or destroys at least 95% of the test VOCs in the incoming air stream.
- Adsorption capacity of the carbon decreases over time. However, even after several years of loading and regeneration, the carbon still retains considerable loading capacity (35-95%), for several VOCs that were analyzed.
- Degradation of photolytically active VOCs is enhanced by increased humidity, increased residence time in the photolytic reactors through recirculation, turbulence or bulb placement, optimized light intensity distribution, and proper wavelength selection.
- Efficiency of the packed bed scrubbers would be enhanced by ensuring that VOCs absorbed by the water phase are rapidly destroyed in the water treatment tank.
- The mist air dispersion units appear to add little to the efficiency of the packed bed scrubbers, or the system as a whole.
- Only a slight amount of the ozone penetrates deeply into the carbon bed; therefore increased activity in the carbon bed might be effected by a modified geometry allowing close contact between carbon and ozone at more frequent intervals.
- System modifications such as pH control and elimination of the second photolytic reactor may be required when treating air streams with high concentrations of chlorinated hydrocarbons.
- Biodegradation may play a major role in the degradation achieved in the carbon bed. Results are preliminary; research is continuing in this area under alternate funding. Findings may provide the key to the functioning of the Terr-Aqua system.
- The CARC replacement solvent N-methyl-2-pyrrolidinone (NMP) is easily removed from the air stream in the packed bed scrubber, and its degradation is enhanced by the addition of hydrogen peroxide and increasing the pH to 9. The addition of hydrogen peroxide and/or increasing the pH of the water treatment tank are low cost modifications expected to increase the degradation of other organic compounds as well.

Hybrid systems clearly have a role in the treatment of air streams typical of those found in paint booth applications. Such air streams are characterized by relatively low concentrations of VOCs, relatively high volumetric flow rates, changing mixtures of VOC components, and irregular or inconsistent flow rates. This research has identified many positive reasons that this system is applicable to this type of exhaust stream; it has also identified many areas for possible system optimization, enhancement, and cost reduction.

Additional funding is needed to confirm these findings by additional experimentation and scale up to the pilot scale system. Funding is also needed to perform long-term (multi-month) testing on the full scale system at Barstow. The primary goals of long term testing would be to determine the effects of continuously alternating loading and regeneration of the carbon bed, and to determine if biodegradation does play a role. These two processing effects cannot be measured on the pilot scale system since it is not in continuous operation.

Numerous theses, papers and publications have resulted, and will continue to result from this work. They are listed in Appendices A - D of this report, and, to facilitate their review, abstracts have been included wherever possible. Details of the research may be found in the original publications or by contacting the authors.

Although SERDP funding was not continued past the second year, an extensive body of knowledge and a unique, state-of-the-art facility have been established and should be utilized. Relationships established between ARL Penn State, the Marine Corps, and Terr-Aqua remain intact as well, and all partners are eager to pursue further efforts. Alternate sources of funding on air treatment and related projects utilizing oxidative oxidation technologies are being sought.

5.0 ACKNOWLEDGMENTS

The Applied Research Laboratory wishes to thank the Strategic Environmental Research And Development Program for funding this research; Ron Vargo, John House and The Marine Corps Logistics Bases for their project leadership, genuine involvement and interest, and financial support; Terr-Aqua Enviro Systems, Inc. for their gift of the pilot scale system and for their workmanship and attention to the design characteristics of the research pilot scale system; and to the Pennsylvania State University engineering students for their professionalism, dedication and support of this project.

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APPENDIX A

PHOTOLYTIC MODELING AND BENCH SCALE RESEARCH

Theses

Spaeder, T. A., *The Effect of Ultraviolet Light and Ozone on Methanol*, Ph.D. Thesis, The Pennsylvania State University (expected August 1996; thesis title and abstract are tentative at this time and may change before publication).

DRAFT ABSTRACT

The photochemical transformation of gas phase methanol was investigated at standard temperature and pressure in a single pass gas phase photochemical reactor equipped with a 700 watt medium pressure mercury lamp (Heraus TQ 718). Photochemically generated ozone was added to the air/methanol matrix to enhance transformation of methanol into formaldehyde. Computer simulation models were also developed which predicted the transformation rate of methanol and its byproducts. Computer simulation results indicate that photochemical transformation only occurred in close (within one bulb diameter) proximity to the TQ 718 lamp. Computer simulations and experimental results correlate well for cases where the TQ 718 lamp was illuminated. Further analysis is underway.

Mallery, M. R., *Numerical Model of Formaldehyde Photo-Oxidation in a Two-Dimensional Flow Field Over Cylindrical UV Light Sources*, M.S. Thesis, The Pennsylvania State University (August 1995).

ABSTRACT

A numerical model has been developed which describes the interaction between the fluid dynamics of a flowing volatile organic compound (VOC) laden gas stream and the photochemical and chemical processes occurring within a photolytic reactor. The gas velocities and chemical species concentrations are predicted as a function of spatial location within the reactor under steady state conditions. The VOCs chosen for study are formaldehyde and methanol, and it is the goal of this research to determine the mechanisms (fluid dynamic, chemical or photochemical) which most directly influence the destruction of formaldehyde in the reactor. It is also the goal of this research to recommend potential design changes to enhance VOC destruction. One design change that is investigated is the use of a titanium dioxide catalyst coated along the reactor walls.

It was discovered through this research that residence time, ozone concentration, and actinic flux are important parameters to consider in the design of a photolytic reactor. It was also found that the TiO_2 heterogeneous photocatalyst has the potential to significantly enhance VOC degradation in the reactor.

Spaeder, T. A., *The Effect of Low-Pressure Mercury Lights on Vapor Phase Ethanol*, M.S. Thesis, The Pennsylvania State University (May 1994).

ABSTRACT

The photolytic destruction of ethanol in air streams illuminated with high purity quartz low-pressure mercury lamps was investigated. A gas tight composite 316 stainless steel and acrylic reactor loop was constructed which allowed for doping ambient air with ethanol, and circulating it past the lamps. Ethanol concentration measurements were recorded when only one 40 watt lamp was illuminated, and again when three 40 watt lamps were illuminated. It was determined that by increasing the actinic flux from 40 watts to 120 watts the overall rate constant for ethanol increased from 8.25E-5/sec to 1.06E-3/sec when corrected for wall loss. Organic chemical intermediates were formed by this process, and depended upon the actinic flux and the residence time in the reactor loop. Finally, it was determined that 7.2mW/CFM of 185 nm radiation increased the kinetic rate constant by over two orders of magnitude.

Young, C. A., "Optimization of Ultraviolet Bulb Configuration in a Photoxidation Chamber," B.S. Thesis, The Pennsylvania State University, (May 1995).

ABSTRACT

The air flow around ultraviolet bulbs in an Air Pollution Control System (APCS) photolytic oxidation chamber is studied using a low speed wind tunnel. The APCS uses photooxidation, water stripping, and an activated carbon bed to eliminate volatile organic compounds (VOCs) produced by a variety of industrial activities. This research uses a flow visualization technique to optimize the first of these mechanisms. The APCS contains two photolytic oxidation chambers with seven shielded ultraviolet bulbs apiece. Bulb and shield orientation and bulb location are studied to determine an optimal configuration for increased residence time and enhance VOC elimination in the chamber. In addition, an analytical two-bulb model is verified both qualitatively with flow visualization and quantitatively with Reynolds number matching and velocity measurements.

Papers and Publications

Heinsohn, R. J., Spaeder, T. A., Albano, M. T., Schmelzle, J. P. and Fetter, R. O., "Ultraviolet and Radical Oxidation of Airborne VOCs," First International Conference on Advanced Oxidation Technologies for Water and Air Remediation," London, Ontario, Canada (June 1994).

ABSTRACT

Airborne VOCs reactions initiated by UV radiation at selected wavelengths from 185 to 308 nm have been studied. A simplified kinetic mechanism is

proposed incorporating photolysis and radical reactions. The concentration of formaldehyde (HCHO) and methanol (CH_3OH) were predicted as a function of time, radiation wavelength, actinic flux and initial ozone concentration. The gas velocity and HCHO concentration were predicted in a gas stream flowing over a UV bulb. Experiments were conducted in which ethanol vapor and air were irradiated by low-pressure mercury bulbs. Ethanol disappeared in an overall first-order manner and an intermediate species, believed to be acetaldehyde, appeared and then disappeared.

Heinsohn, R. J., Spaeder, T. A., Albano, M. T., Schmelzle, J. P., Fetter, R. O. and Farson, D. F., "Ultraviolet and Radical Oxidation of Airborne Volatile Organic Compounds," Paper 45c, AIChE Summer Meeting, Seattle (1993).

ABSTRACT

Same as paper above.

Mallery, M. R., and Heinsohn, R. J., "Numerical Model of Formaldehyde Photo-Oxidation in a Two-Dimensional Flow Field Over Cylindrical UV Light Sources," ACS Emerging Technologies in Hazardous Waste Management VII, Atlanta, GA (September 1995).

EXTENDED ABSTRACT

Introduction

Passage of the Clean Air Act Amendments by President Bush in 1990 is placing more stringent control on VOC emissions. These emerging regulations are forcing industries to reduce VOC emissions through new manufacturing techniques or through the use of air pollution control equipment. An emerging air pollution control technology is the use of ultraviolet (UV) photochemical and radical oxidation to destroy pollutant VOCs in process gas streams. A commercial system based in part on this technology has been developed and a pilot scale version has been installed at the Applied Research Laboratory (ARL) at The Pennsylvania State University. Research is currently being performed with the pilot scale system to determine the systems effectiveness in removing different classes of VOCs and to recommend design improvements that enhance VOC destruction throughout the system. A numerical model of the photolytic reactor in the pilot scale system has been developed in support of this research effort.

The numerical model describes the interaction between the fluid dynamics of a flowing volatile organic compound (VOC) laden gas stream and the photochemical and chemical processes occurring within the photolytic reactor. The gas velocities and chemical species concentrations are predicted as a function of spatial location within the reactor under steady state conditions. Formaldehyde (HCHO) in moist air with trace amounts of ozone is used to evaluate the reactor performance. The effects of residence time, ozone inlet concentration and actinic flux on formaldehyde destruction in the reactor were investigated.

Model Description

Figure 1 provides the reactor configuration analyzed in this study. The reactor is a rectangular duct containing two cylindrical medium-pressure mercury arc lamps (Heraeus Amersil TQ718) which emit electromagnetic radiation over the wavelength range from 238 to 579 nm. An air stream containing formaldehyde, methanol, ozone and water vapor enters the reactor and passes perpendicular to the cylindrical lamp axes.

The mathematical model of the reactor was constructed using Harwell (CFDS)-FLOW3D, which is a Computational Fluid Dynamics (CFD) package developed by Harwell Laboratory in the United Kingdom. The photolytic reactor model combines: (1) a description of the light intensity distribution in the reactor, (2) a description of the reaction kinetics for HCHO destruction in air in the presence of UV light and (3) a description of the velocity field through the reactor. The chemical and photochemical reaction processes occurring within the photolytic reactor are modeled with the addition of a FORTRAN 77 subroutine.

The model analyzes the photolytic reactor in two dimensional space with a radiation field emitted by the TQ718 lamps that is purely radial. It is also assumed that HCHO and O_3 are the only chemical species which contribute significantly to light attenuation in the reactor. The light intensity distribution in the reactor based on these assumptions is given by the Beer-Lambert Law:

$$I_r = \frac{r_o I_{ro}}{r} e^{-(r-r_o)\sum [C]\sigma} \tag{1}$$

Subsequently, the photolysis rate constants for formaldehyde, ozone and hydrogen peroxide are calculated with equation (2) where a summation is provided to account for the dominant wavelengths emitted by the TQ718 lamp:

$$k = \frac{r}{r_o} \sum_{\lambda_1}^{\lambda n} \sigma(\lambda, T) \phi(\lambda, T) e^{-(r-r_o)\sum [C]\sigma} J(\lambda) \tag{2}$$

Twenty-three chemical reactions involving 14 chemical species are analyzed in the model. This is a simplified kinetic model developed based on over 56 chemical reactions for 21 chemical species that were compiled from the literature to describe gas phase oxidation of HCHO in the presence of UV light (Schmelzle, 1994 and Albano, 1994). The kinetic mechanisms were incorporated into the flow field model by introducing the species mass conservation equation for each of the following chemical species: HCHO, CH_3OH, $OH^\bullet$, $H^\bullet$, $HO_2^\bullet$, $O(^3P)$, $O(^1D)$, H_2O_2, O_3, HCHO and CO. The kinetic mechanisms which lead to generation or removal of a given species were incorporated as source/sink terms, symbolized by S, in the species mass conservation equation given below:

$$\nabla \cdot (\rho UC) - \nabla \cdot ((\frac{\mu_T}{\sigma_s} + \rho D)\nabla C) = S \tag{3}$$

The flow field in the reactor was modeled with the Navier-Stokes and mass conservation equations by assuming that a turbulent air stream entering the reactor was a Newtonian incompressible fluid with constant properties. The turbulence was analyzed using the k-ε turbulence model. The final model includes the numerical solution of 16 equations for 16 unknowns.

Results

The goal of the current modeling effort was to describe the physical and chemical processes occurring in a photolytic reactor and determine courses of action to increase the efficiency of the reactor. HCHO is destroyed in the reactor by two routes: direct photolysis and radical oxidation by $OH^\bullet$. It was found that destruction by photolysis is an order of magnitude slower than by $OH^\bullet$ radical attack. For this reason methods were researched to increase the $OH^\bullet$ concentration in the reactor. It was found that photolysis of O_3 leads to the production of $OH^\bullet$ radicals in the presence of water vapor. Parametric studies were therefore performed with varying ozone concentrations from 75 ppm to 300 ppm. It was found, as was expected, that the destruction of HCHO increased with increasing O_3 inlet concentrations. However, 90% of the ozone input into the reactor was discharged out the reactor outlet. This implies that an ozone scrubber would be required with a photolytic reactor design employing ozone to enhance VOC oxidation rates.

The effect of light intensity on HCHO destruction was also studied. Increasing the light intensity not only increases the HCHO photolysis rate but also the photolysis of O_3. A 10 fold increase in light intensity significantly increased HCHO oxidation. However, Figure 2 shows that the light intensity emitted by the lamps drops off with distance from the bulbs. Therefore proper arrangement of bulbs in the reactor to optimize the light intensity distribution would be beneficial. Several smaller wattage bulbs would be more efficient than one high intensity bulb in the middle of the reactor.

Next the interaction between gas stream advection (hence residence time) and the chemical reaction rates were investigated. It was found that when the chemical reaction rates are much faster than the gas stream advection, the species concentration distributions are unaffected by the flow field. An example is the $OH^\bullet$ concentration distribution in the reactor shown in Figure 3. The distribution mimics the light intensity profile emitted by the TQ718 lamps shown in Figure 2. HCHO (shown in Figure 4) and O_3 concentration distributions in the reactor, on the other hand, are influenced strongly by the reactor flow field. Figure 4 shows an overlay of the reactor velocity field on the HCHO concentrations contours. The concentration contours follow the velocity vectors which are overlaid on top. The acceleration of flow over the top surfaces of the bulbs result in lower destruction of HCHO whereas the recirculating regions behind the bulb surfaces lead to high HCHO oxidation rates. The rates of advection were varied in the reactor by varying the reactor inlet velocities from 0.5 m/s to 3.5 m/s. The highest HCHO removal occurred for the lowest inlet velocity case with negligible destruction occurring for an inlet velocity of 3.5 m/s. An improvement in the reactor design would therefore be to increase the gas stream residence time in the reactor. This can be accomplished by increasing recirculation in the reactor.

Based on the results of this study, a photolytic reactor design should have close placement and arrangement of UV bulbs to optimize light intensity distribution. The UV lamps should also be chosen to maximize power output in the wavelength ranges that produce photolysis of the target VOC and ozone. If the bulbs are placed too far apart, part of the gas stream will remain essentially untreated due to the decrease of light intensity (hence $OH^{\bullet}$ radical concentration) with distance from the bulb. A photolytic reactor design should also optimize recirculation of the process gas stream within the reactor to increase gas stream residence time.

Nomenclature

C	Species Concentration	U	Gas Velocity
D	Molecular Diffusion Coefficient	ϕ	Quantum Yield
I_{ro}	Light Intensity at surface of bulb	ρ	Gas Density
$J(\lambda)$	Actinic Flux	σ_S	Turbulent Prandtl Number
r	Distance from bulb	μ_T	Turbulent Viscosity
r_o	Bulb radius	σ	Absorption Cross-section

Mallery, M. R., and Heinsohn, R. J., "Numerical Model of a Photolytic Reactor for VOC Destruction," A&WMA Conference on Emerging Solutions to VOC and Air Toxics Control, Clearwater, FL (February 1996). Also to be published in the proceedings from this symposium.

ABSTRACT

Passage of the Clean Air Act Amendments by President Bush in 1990 is placing more stringent control on VOC emissions. These emerging regulations are forcing industries to reduce VOC emissions through new manufacturing techniques or through the use of air pollution control equipment. An emerging air pollution control technology is the use of ultraviolet (UV) photochemical and radical oxidation to destroy pollutant VOCs in process gas streams. A commercial system based in part on this technology has been developed and a pilot scale version has been installed at the Applied Research Laboratory (ARL) at The Pennsylvania State University. Research is currently being performed with the pilot scale system to determine the systems effectiveness in removing different classes of VOCs and to recommend design improvements that enhance VOC destruction throughout the system. A numerical model of the photolytic

reactor in the pilot scale system has been developed in support of this research effort.

The numerical model describes the interaction between the fluid dynamics of a flowing volatile organic compound (VOC) laden gas stream and the photochemical and chemical processes occurring within the photolytic reactor. The gas velocities and chemical species concentrations are predicted as a function of spatial location within the reactor under steady state conditions. Formaldehyde (HCHO) in moist air with trace amounts of ozone is used to evaluate the reactor performance. The effects of residence time, ozone inlet concentration and actinic flux on formaldehyde destruction in the reactor were investigated.

It was found that the addition of ozone at the front end of the reactor significantly enhanced HCHO destruction. However, a significant portion of the ozone remained unreacted at the reactor outlet. HCHO destruction was also enhanced by increased residence times and efficient distribution of electromagnetic radiation from UV sources.

Spaeder, T. A. and Traband, M. "LEAD Decision Paper," Applied Research Laboratory, Manufacturing Science Department, State College, PA (1991).

NOTE

One portion of the LEAD Decision Paper presents a discussion and cost comparison of the hybrid advanced oxidation treatment technology to other, more conventional air treatment techniques such as carbon adsorption and thermal oxidation. This portion of the paper has also been condensed and is included as "Appendix D: Economic Cost Analysis" in Spaeder's M.S. Thesis listed above.

The evaluation is based upon the initial capital costs of procuring, installing and permitting the devices as well as the projected recurring costs (operation and maintenance). The costs were compiled based on vendor quotes, energy and labor costs provided by Letterkenny Army Depot, and criteria from the EPA. A summary of these costs, including a total ten year cost for the seven devices evaluated, is included.

Based only this study, it was determined that, although initial capital investment for the hybrid advanced oxidation system is high, recurring costs are low, and over a ten year period, the average annual cost for this technology is less than that of the other systems evaluated.

Spaeder, T. A., "Experimental Studies of an Ethanol Air Flow Subjected to UV Light," Air & Waste Management Association 89th Annual Meeting and Exhibition, Cincinnati, OH (June 1994).

INTRODUCTION

Airborne volatile organic compounds (VOCs) emissions are generated from a large number of manufacturing processes including coating application, pharmaceutical production and petrochemical manufacturing. The United States Environmental Protection Agency (USEPA) estimates that hundreds of millions of tons of VOCs are emitted to the atmosphere by industries each year in the United States. VOCs released into the atmosphere react with sunlight and create photochemical smog, oxidants and other pollutants. Many manufacturing processes which liberated VOCs in the past have made production changes which eliminate or lower the amount of VOCs liberated; however, some manufacturing processes cannot eliminate using VOCs or reduce their emissions by solvent substitution. These emission sources typically add "tail pipe" air pollution control systems (APCS) to reduce their emissions. APCS are bulky and costly pieces of equipment which add no value to the product line being produced. Because of this, industries which are forced to install APCS are constantly looking for more cost effective APCS solutions.

In the last eight years a new technology has come to market which uses ultraviolet light, ozonated water scrubbing and regenerating carbon adsorption to destroy VOCs on site, without the generation of any secondary hazardous waste.

This new technology has approximately the same initial capital installation cost as compared to other technologies ($35/SCFM), but the recurring operating costs are one tenth of competing technologies. Therefore a great deal of interest has been expressed about this type of APCS. this research focuses on the ultraviolet light reactors which are employed in this APCS.

Specifically, this research will investigate the destruction of an ethanol-laden air stream to 40 watt low-pressure mercury lights. The following topics will be investigated:

1. kinetic mechanisms which lead to the destruction of ethanol,
2. interaction of ultraviolet light with ambient air for the generation of radicals,
3. design, construct and monitor a multi-pass closed loop ultraviolet light reactor for exposure of VOC-laden air to ultraviolet light,
4. disappearance of ethanol will be monitored, and rate constants will be determined for two actinic fluxes.

Spaeder, T. A., "Experimental Studies of an Ethanol Air Flow Subjected to UV Radiation," Air and Waste Management Air Toxics Conference, Raleigh-Durham, NC (June 1994).

ABSTRACT

Same as paper above.

APPENDIX B

PACKED BED SCRUBBER AND WATER REGENERATION

Theses

Striebig, B. A., *Optimization of N-methyl-2-pyrrolidinone Removal in a Chemical Absorption Reactor*, Ph.D. Thesis, The Pennsylvania State University (expected August 1996; thesis title and abstract are tentative at this time and may change before publication).

DRAFT ABSTRACT

N-methyl-2-pyrrolidinone (NMP) is a high molecular weight solvent with a relatively low vapor pressure. NMP is used to replace highly volatile organic compounds (VOCs) in surface coatings. The Marine Corps Multi-Commodity Maintenance Centers $(MC)^3$ have incorporated NMP in a reformulated Chemical Agent Resistant Coating (CARC). An air pollution control system was installed at $(MC)^3$ in Barstow, CA to treat exhaust air streams from CARC application processes. The air pollution control system incorporates an ultra-violet reactor, an aqueous absorption reactor, an ozonated water recycle-tank for the scrubbing liquor, and a carbon sorption bed. This report focuses on the aqueous phase reactions, and absorption processes which occur in the air pollution control system.

A constantly stirred tank reactor was used to determine a chemical mechanism for the aqueous phase reactions of NMP with ozone and hydrogen peroxide. The pH of the reactor, the ozone addition rate, and the hydrogen peroxide addition rate were optimized to achieve the most rapid oxidation of NMP. A chemical model for the reaction of NMP, ozone and hydrogen peroxide was determined and used in analytical models of chemical absorption processes.

Analytical models of the chemical absorption reactor predicted the effects optimized chemical oxidation reactions would have upon the removal efficiency of NMP from an exhaust air stream. The analytical models compared the removal efficiency of NMP in a pure absorption process to an optimized chemical absorption process. The analytical model was also used as a design aid in the scale down of the bench scale chemical reactor. Experiments were conducted in both bench and pilot scale chemical absorption reactors to evaluate the validity and practicality of using the analytical models in the design of a chemical absorption reactor for the removal of NMP from an exhaust air stream.

Experiments were run to simulate the conditions of the air pollution control system in Barstow, CA and the optimized conditions as determined through the analytical studies. The optimized conditions were simulated in the bench-top chemical absorption reactor to verify the effects which the chemical reactions have upon the absorption process. The pilot scale system was optimized through the addition of hydrogen peroxide and by maintaining an elevated pH to evaluate the actual NMP removal efficiency of the pilot scale absorption reactor. This paper will present the findings of these studies.

It was concluded that chemical absorption processes are viable methods for the continuous removal of N-methyl-2-pyrrolidinone from an exhaust air stream.

Further studies should examine the further oxidation of the by-products of NMP, and the potential formation of precipitates in the aqueous phase. Future research may find synergistic effects of chemical solubilities and reactions of other solvents treated by the air pollution control system through the creation of hyroxl radical chemistry at the optimized conditions.

Papers and Publications

Striebig, B. A., Schneider, J. M., Watt, L. C., Vargo, R., "Environmental Impact and Treatment of Reformulated Chemical Agent Resistant Coatings," 2nd Aerospace Environmental Technology Conference, Huntsville, AL (August 1996). Abstract also to be published in the proceedings from this symposium.

ABSTRACT

The 1990 Clean Air Act provided an incentive to replace highly volatile organic compounds (VOCs) with less volatile solvents. The Marine Corps Multi-Commodity Maintenance Centers $(MC)^3$ have taken the initiative to reformulate the currently used Chemical Agent Resistant Coatings (CARC) in order to reduce the VOC content. The primary solvents used in the reformulated CARC are water and N-methyl-2-pyrrolidinone (NMP). Because NMP has a very low vapor pressure and high molecular weight, it does not partition rapidly to the gas phase, unlike current industrial solvents. Thus coatings which use water and NMP are beneficial in terms of pollution prevention and are less toxic. However, air treatment systems must be capable of removing NMP from exhaust air streams in addition to solvents currently used in the CARC application process.

The Applied Research Laboratory at The Pennsylvania State University has investigated a hybrid air pollution control system to treat an NMP laden air stream. The system has been described in "Air Pollution Control System (APCS) Research - an Iterative Approach to Developing Affordable Systems" (Watt, 1994) presented at the First Aerospace Environmental Technology Conference. This research was performed concurrently with the reformulation of the CARC coatings to ensure current air treatment systems installed at $(MC)^3$ facility in Barstow, California were capable of adequately removing NMP from exhaust air streams. Bench scale and pilot scale studies focused on the absorption of NMP into an aqueous phase and subsequent destruction of the NMP through advanced oxidation processes.

NMP was effectively removed from an air stream using the hybrid system APCS. The hybrid design was optimized for the removal and destruction of NMP from exhaust air streams. Advanced oxidation processes destroyed NMP in the aqueous phase. the products of the oxidation reactions of NMP were determined. The results of these studies show the reformulated CARC is a beneficial step in pollution prevention since the VOC content of the coating is reduced and the replacement solvent NMP can be removed using existing air treatment technologies installed at the $(MC)^3$ facility.

APPENDIX C

CARBON ADSORPTION AND REGENERATION

Theses

Dusenbury, J.S., *Ozone Enhanced Biodegradation of Volatile Organic Compounds in a Granular Activated Carbon Bed,* PhD. Thesis, The Pennsylvania State University (expected May 1997; thesis title and abstract are tentative at this time and may change before publication).

DRAFT ABSTRACT

The Pennsylvania State University is researching an advanced oxidation system, which includes an air-phase photolytic chamber, an air/water stripping tower, and granular activated carbon (GAC) beds, for controlling volatile organic compounds (VOCs).

A laboratory-scale experimental procedure has been employed that simulates certain aspects of the carbon beds at several full-scale installations. The laboratory apparatus has been used to characterize the loading capacity and mass transfer zone of selected VOCs onto coconut shell GAC. This same GAC bed has then been placed in series with an ultraviolet/O_3 reactor in order to regenerate the loaded GAC. Finally this experimental apparatus has been used to study biodegradation of the VOCs within the GAC bed.

VOC loading tests revealed that the adsorption of methylisobutyl ketone (MIBK) was characterized by a well-behaved mass transfer zone. Upon exposure to UV/O_3, desorption and/or destruction of the MIBK and other VOCs occurred most prominently within the first inch of the GAC bed. This correlated accordingly with the penetration of advanced oxidants into the GAC bed, which also occurred most significantly in the bed's first inch. However, the amount of oxidant penetration increased with time. The removal of oxidants from air by GAC was accompanied by a decrease in mass of the GAC surface. The ability of oxidants to penetrate a GAC bed was altered when the bed was loaded with a VOC.

Filamentous growth has been observed in a GAC bed which has been continuously loaded with benzene for over 1 month. This growth is green-brown in color and causes agglomeration of 5 centimeter aggregates within the GAC bed. At this time, it is anticipated that this bed will be further investigated to determine the efficiency of the VOC removal by the biologically active GAC. The effect of mass loading with respect to influent concentration and flow rate will be evaluated, as will the effect of VOC loading/ozonation cycles on the system.

Paulsen, Paul D., *Diffusion and Adsorption of Volatile Organic Compounds onto Activated Carbon,* PhD. Thesis, The Pennsylvania State University (expected August 1997; thesis title and abstract are tentative at this time and may change before publication).

DRAFT ABSTRACT

This research has sought to characterize the way Volatile Organic Compounds (VOCs) are loaded onto individual Granular Activated Carbon (GAC) grains, and how these carbon grains can be regenerated for reuse. Fundamental understanding has been sought regarding how VOCs diffuse through the pores of the GAC, how the affinity of the VOCs for the carbon surface affects regeneration, and how temperature and ozonation alter this affinity. This investigation has supported Pennsylvania State University research on a Terr-Aqua pollution control system that uses GAC adsorption of VOCs with ozone regeneration as a unit process.

A Thermogravimetric Analyzer (TGA) controls sample temperature and VOC concentration while collecting loading data. Data taken when sample has reached steady state establishes the equilibrium relationship between adsorbed and vapor phases at different temperatures and concentrations. A pore diffusion model has been developed to describe the penetration and loading of VOCs onto GAC. Numerical solution of the resulting partial differential equation allows for calculation of effective diffusion coefficients from loading data. Using these parameters, pore diffusion model predicts desorption of VOCs from carbon grains under different environments. Ozonation of sample reduces the affinity of the VOC for the carbon surface and is solely modeled through alteration of the equilibrium relationship between adsorbed and vapor phases of the VOC.

Singh, J., *Characterization of GACs Regenerated Using Advanced Oxidation Processes*, M.S. Thesis, The Pennsylvania State University (May 1995).

ABSTRACT

Air emissions present a major threat to society. These emissions can originate from air stripping processes, hazardous waste incinerators, carbon regeneration plants, municipal landfill sites, dry cleaning facilities and wastewater treatment plants. Industrial and manufacturing processes that employ organic solvents, such as pharmaceutical production, spray booth coating applications, and petrochemical manufacturing, constitute another major source of airborne volatile organic contaminants (VOCs) and hazardous air pollutants (HAPs).

VOCs released into the atmosphere react with sunlight to create photochemical smog, oxidants and other pollutants. Smog not only affects visibility, but is also known to be damaging to plants and detrimental to human health. Thus, there is a need to control these emissions into the atmosphere.

In the past decade an innovative process to remove VOCs from process gas streams has become commercialized. This system operates at ambient temperature and ambient pressure. It consists of three processes occurring in series;

1) UV photolysis and free radical generation in the gas phase,
2) Wet scrubbing with ozonated water,

3) Adsorption in granular activated carbon (GAC) with regeneration using advanced oxidation processes.

The focus of this study has been to study and characterize the adsorption and regeneration characteristics of the GAC involved in this process. This GAC undergoes daily cycles of VOC loading followed by ozone/UV regeneration (also known as advanced oxidation (AO) regeneration). This frequent cycling prevents the build-up of VOCs to levels that cause the effluent concentration to exceed standards. The GAC thus serves as a "capacitor" for the VOCs, which facilitates the necessarily long reaction times for the ozone and UV generated radicals to oxidize the retained VOCs. However, under the effect of such a strong oxidizing atmosphere, the surface of the activated carbon itself could potentially also be oxidized. This could affect its adsorption capacity during subsequent cycles.

The results of this study suggest that not all of the VOCs that are adsorbed onto the surface of the GAC during the loading stage are removed during subsequent AO regeneration. This seems to affect a lot of the other results obtained. A considerable reduction is observed in the pore volumes and surface areas of the regenerated samples. There is a simultaneous reduction in the adsorption capacity for VOCs. These reductions are greater in the case of polar compounds than in the case of less polar or non-polar compounds. An increase in surface oxygen content is also observed.

These results can have a significant effect on the design of the current system. The results indicate that within the present configuration, GAC can survive many more AO regenerations than it could thermal oxidation regenerations. With AO regeneration, the pore structure and adsorption capacity is not degraded completely even after several years of use. The adsorption capacity for polar compounds is reduced about the same as could be expected from pore structure degradation, and oxygenation of the GAC surface apparently plays a role. However, the residual capacity is still significant and design should be based on this capacity rather than the capacity of a virgin GAC. The rate of the decrease in adsorption capacity needs to be investigated further.

Papers and Publications

Cannon, F. S., J. S. Dusenbury, P. D. Paulsen, Jyoti Singh, D. Mazyck, D. Maurer, "Advanced Oxidant Regeneration of Granular Activated Carbon for Controlling Air-Phase VOCs," Accepted for publication in *Ozone Science and Engineering* (1996).

ABSTRACT

The Pennsylvania State University is researching an advanced oxidation (AO) system for controlling volatile organic compounds (VOCs) (CANNON et al. 1994). The system includes an air-phase photolytic chamber, an air/water stripping tower, and granular activated carbon (GAC) beds, and the work herein evaluated the GAC beds.

Field GACs have been evaluated, which had previously been loaded with VOCs and regenerated with AO for several years at several full scale installations. Full scale response was then simulated in laboratory-scale experiments.

Results revealed that following 500 to 1000 daily loading and regeneration cycles, one field GAC lost 35 % of its micropore volume, and 17-35% of its capacity to adsorb several VOCs. Under another condition, for a Furniture Coating GAC, 80% of the micropore volume was lost after several years of loading and reactivation cycles, and 23 to 63 % of the VOC adsorption capacity was lost.

Laboratory results revealed that prolonged AO regeneration destroyed or desorbed most of the MIBK within the first inch of a GAC bed. AO regeneration also removed a fourth of the MIBK in the next five inches of the packed GAC bed. Several byproducts were created by the MIBK destruction, which generally contained one-to-three fewer carbon atoms than MIBK did, and also contained more oxygen functional groups.

Concurrent to these experiments, thermogravimetric analysis (TGA) tests evaluated the rate and extent of MIBK adsorption onto virgin GAC, and revealed that the MIBK adsorption capacity was fairly insensitive to the ranges of concentration and temperature that were employed. A modeling analysis of the diffusion characteristics onto virgin GAC revealed that during the time frame of three to five hours, the mass transfer rate appeared to be governed by restricted diffusion.

Cannon, F. S., J. S. Dusenbury, P. D. Paulsen, Jyoti Singh, D. Mazyck, D. Maurer, "Advanced Oxidant Regeneration of Granular Activated Carbon for Controlling Air-Phase VOCs," Advanced Oxidation International Conference, Nashville, TN (February 1995).

ABSTRACT

Same as the paper above.

Dusenbury, J., and Cannon, F. S., "Advanced Oxidant Regeneration of Granular Activated Carbon for VOCs," 22nd Biennial Conference on Carbon, San Diego, CA (July, 1995). Also to be published in the proceedings from this symposium.

ABSTRACT

Same as the following paper.

Dusenbury, J., and Cannon, F. S., "Advanced Oxidant Reactivity Within Granular Activated Carbon Beds for Air Pollution Control," Submitted to *Carbon Journal* (1995).

ABSTRACT

The Pennsylvania State University is researching an advanced oxidation system, which includes an air-phase photolytic chamber, an air/water stripping tower, and granular activated carbon (GAC) beds, for controlling volatile organic compounds (VOCs).

A laboratory-scale experimental procedure has been employed that simulates certain aspects of several full-scale installations. The laboratory apparatus has been used to characterize the loading capacity and mass transfer zone of selected VOCs onto coconut shell GAC. This same GAC bed has then been placed in series with an ultraviolet/O_3 reactor in order to regenerate the loaded GAC.

VOC loading tests revealed that the adsorption of Methyl isobutyl ketone (MIBK) was characterized by a well-behaved mass transfer zone. Upon exposure to UV/O_3, desorption and/or destruction of the MIBK and other VOCs occurred most prominently within the first inch of the GAC bed. This correlated accordingly with the penetration of advanced oxidants into the GAC bed, which also occurred most significantly in the bed's first inch. However, the amount of oxidant penetration increased with time. The removal of oxidants from air by GAC was accompanied by a decrease in mass of the GAC surface. The ability of oxidants to penetrate a GAC bed was altered when the bed was loaded with a VOC.

Singh, J., and Cannon, F. S., "Characterization of Advanced Oxidation Regenerated GACs," ASCE, Environmental Engineering Division, Conference on Innovative Technologies for Site Remediation and Hazardous Waste Management, Pittsburgh, PA (July, 1995).

ABSTRACT

This paper explores the effects of regeneration by means of advanced oxidation involving UV and ozone, on several properties of granular activated carbons (GACs). The effects of reductions in surface areas and pore volumes, and surface oxidation due to this process of regeneration, on adsorption capacities of some model VOCs is investigated.

As a result of this study, the following conclusions were arrived at:

- The APCS (air pollution control system) regeneration process does not remove all the VOCs that accumulate during the loading stage. Following hundreds of cycles of loading and regeneration inside the APCS, some loading of VOCs builds up on the surface of GAC. This loading is not

uniform from grain to grain of the carbon, and its presence interferes somewhat with further adsorption during subsequent loading stages.

- The adsorption capacities of the carbons for several types of VOCs decrease following several hundred regeneration cycles. However, considerable capacity remains, and the GAC could usefully function in this reduced-capacity mode for a large number of further regeneration cycles.
- Pore volumes and surface areas of the carbon also decrease after several hundred regeneration cycles, but remained remarkably high relative to what could have been expected following as many thermal reactivation cycles.
- There is an increase in the oxygen content of the carbons following several hundred regeneration cycles.

APPENDIX D

PILOT SCALE DATA AND PROJECT OVERVIEW

Reports

Schneider, J. M., "Treatment of Airborne Volatile Organic Compounds (VOCs) in a Hybrid Pilot Scale System: Phase I - Baseline Studies," Applied Research Laboratory, Manufacturing Technology Department, State College, PA (1996).

DRAFT ABSTRACT

Baseline studies have been performed on a 2500 scfm pilot scale hybrid air treatment system as part of the research sponsored by the Strategic Environmental Research and Development Program (SERDP) and the Marine Corps Multi-Commodity Maintenance Centers $(MC)^3$. This hybrid system combines photolytic degradation, counter-current packed bed aqueous scrubbing, and carbon adsorption.

Approximately 30 gallons of VOCs and HAPs, consisting of ethanol, methylethyl ketone, ethylbenzene, and have been treatment tested in the system. As configured, the pilot scale system removed better than 95% of the VOCs tested.

- Of the four compounds tested, only trichloroethylene (TCE) showed significant photolytic degradation.
- All compounds tested were rapidly absorbed into the water phase in the packed bed scrubbers. Polar compounds were absorbed for a longer period of time than non-polar compounds. Water phase oxidation of the VOCs was not rapid enough to keep up with the input of fresh VOCs into the system.
- The mist air dispersion units appeared to have no measurable treatment efficiency.

The baseline findings are significant and point toward several possible system alterations to increase system efficiency and reduce system cost. Additional studies are recommended to test possible alterations before scale-up to new commercial systems.

Papers and Publications

Schneider, J. M., Striebig, B., Watt, L. C., "Treatment of VOC-Laden Air Using a Pilot Scale Hybrid System," A&WMA Conference on Emerging Solutions to VOC and Air Toxics Control, Clearwater, FL (February 1996). Also to be published in the proceedings from this symposium.

ABSTRACT

The Strategic Environmental Research and Development Program (SERDP) and the Marine Corps Multi-Commodity Maintenance Centers $(MC)^3$ have sponsored research on a 2500 cfm pilot scale hybrid air treatment system at The Applied Research Laboratory, The Pennsylvania State University. This hybrid system combines photolytic degradation, counter-current packed bed scrubbing, and carbon adsorption to treat a variety of airborne VOCs and HAPs at ambient temperature. In addition, the water and carbon are

regenerated in-situ using advanced oxidation processes, eliminating secondary waste streams.

The pilot scale system has been in operation for over one year. Solvents typically present in Marine Corps coatings have been treated in the system. The performance of each individual system component has been determined for alcohols, hydrocarbons, ketones, and chlorinated solvents. System performance relative to a solvent's chemical functionality and physical attributes has been explored.

This paper will present the findings of these studies and show that hybrid systems have a place in the treatment of exhaust air streams characterized by relatively low concentrations of VOCs, relatively high volumetric flow rates, changing VOC composition, and irregular or inconsistent flow rates.

Schneider, J. M., Striebig, B., Watt, L. C., "Treatment of VOC-Laden Air Using a Pilot Scale Hybrid System," 2nd Aerospace Environmental Technology Conference, Huntsville, AL (August 1996). Abstract also to be published in the proceedings from this symposium.

ABSTRACT

Same as above paper.

Striebig, B. A., Dusenbury, J., Heinsohn, R. J., Mallery, M., Schneider, J. M., Spaeder, T., "Pilot Scale Analysis of Advanced Oxidation Processes in a Hybrid Air Pollution Control System," International Chemical Oxidation Association's 6th Annual Symposium on Chemical Oxidation: Technology for the Nineties, Nashville, TN (April 1996).

ABSTRACT

With the passage of the 1990 Clean Air Act, advanced oxidation processes have gained acceptance as plausible alternatives for treating a variety of industrial air and waste water streams. These advanced oxidation processes are very attractive when contaminant compositions and concentrations in the air stream vary widely making typical catalytic incineration devices costly in terms of fuel and potential catalyst fouling. The Strategic Environmental Research and Development Program (SERDP) and the Marine Corps Multi-Commodity Maintenance Centers (MC^3) have sponsored research on a 2500 scfm pilot scale hybrid air treatment system at The Applied Research Laboratory, The Pennsylvania State University.

The hybrid system has been used at the pilot scale and commercial level to successfully remove a variety of volatile and semi-volatile organic compounds. The pilot scale system has been in operation at The Applied Research

Laboratory for over one year. The results of bench scale experimentation, numerical modeling, and pilot scale evaluation were combined to describe the removal mechanisms and oxidative degradation of a variety of organic compounds. The performance of the system was evaluated for solvents typically present in Marine Corps surface coatings, including alcohols, hydrocarbons, ketones, acetates and chlorinated solvents. The active removal mechanism in the hybrid system was found to be related to the solvent's chemical functionality and physical attributes. The hybrid air treatment system consisted of three unique components; gas-phase photolytic reaction chambers, aqueous chemi-absorption reactors, and carbon absorption beds which were regenerated in-situ through ozonated air.

The performance of the *photolytic reactor* in the pilot scale system was investigated using numerical modeling and experimental measurement of the contaminant fore and aft of the reactor to determine the removal efficiency of the current design and to make recommendations to enhance oxidation in future reactor applications. The numerical model described the interaction between the fluid dynamics of a volatile organic compound laden gas stream and the photochemical and chemical processes occurring within the photolytic reactor. The model indicated that the efficiency of the reactor was a function of the residence time of the organic contaminant, the positioning of the bulbs, the intensity of the light, and the concentration of ozone within the reactor. Experimental findings showed chlorinated compounds were converted rapidly in the photolytic reactor. Increased residence time increased the efficiency of the photolytic reactor as suggested by the model. After exiting the photolytic reactor, the air stream was passed through a series of aqueous chemi-absorption reactors for removal of polar compounds.

The aqueous *chemi-absorption reactor* consisted of a packed tower for absorption of the contaminants into the aqueous phase and an ozonation tank for oxidation of the organic contaminants. The aqueous reactor was modeled analytically and results showed that the removal rate of the contaminant from the air stream was a function of the physical properties of the organic contaminant and the rate of oxidation of the contaminant in the liquid phase. Experimental findings indicated that polar compounds could be removed from the air stream, however the rate of oxidation was slow and allowed the contaminant to be stripped back into the air stream when ozone alone was used as an oxidant. Oxidation rates in the literature were increased by the addition of hydrogen peroxide into the scrubbing liquid to create hydroxyl radicals which react more rapidly to oxidize the contaminant. The addition of hydrogen peroxide aided in the oxidation of one organic contaminant, N-methylpyrrolidinone. The aqueous reactor was capable of removing polar compounds from the air stream and dampening the concentration variations of the contaminant in the air stream. This concentration peak dampening effect was important in providing even distribution of the organic contaminants onto the carbon beds.

The *carbon bed* was found to remove a variety of solvents of interest.. Ozone was found to penetrate into the carbon bed so that oxidation of the contaminants could occur, and the oxidant penetration depth increased in the bed with increased oxidant exposure time. Regeneration of the carbon bed was capable of removing 60 to 85 percent of the VOCs at depth of 0.5 to 1 inch into the carbon bed.

The organic concentrations in the air exiting the carbon bed was measured and the removal efficiency of the overall hybrid system was greater than 95% for the compounds of interest. The hybrid air pollution control technology was effective in removing volatile and semi-volatile organic compounds from the exhaust air streams. This paper will present the findings of these studies. Addition of hydroxyl radical producing oxidants in the gas and aqueous phases, and optimization of the air flow field may significantly reduce the costs of the hybrid systems in future applications. The reactor components operated synergistically to provide a VOC treatment alternative which can be operated at ambient temperatures using advanced oxidation processes and eliminate the generation of secondary waste streams.

Watt, L. C., Cannon, F. S., Heinsohn, R. J., Spaeder, T. A. "Air Pollution Control System Research: An Iterative Approach to Developing Affordable Systems," Defense Manufacturing Conference, San Francisco, CA (December 1993); and Aerospace Environmental Technology Conference, Huntsville, AL (August 1994).

ABSTRACT

This paper describes a Strategic Environmental Research and Development Program (SERDP) funded project led jointly by the Marine Corps Multi-Commodity Maintenance Centers $(MC)^3$, and the Air and Energy Engineering Research Laboratory (AEERL) of the USEPA. The research focuses on paint booth exhaust minimization using recirculation, and on volatile organic compound (VOC) oxidation by the modules of a hybrid air pollution control system. The research team is applying bench, pilot and full scale systems to accomplish the goals of reduced cost and improved effectiveness of air treatment systems for paint booth exhaust.

APPENDIX E

CARC MATERIAL SAFETY DATA SHEETS

MATERIAL SAFETY DATA SHEET
FOR COATINGS . RESINS AND RELATED MATERIALS
DATE OF PREPARATION-11/21/90
MSDS REVISION

MANUFACTURER,S NAME : HENTZEN COATINGS, INC.
ADDRESS : 6937 WEST MILL ROAD
ADDRESS : P.O. BOX 18642
CITY,STATE : MILWAUKEE, WISCONSIN 53218
NAME OF PREPARER: Jane Freeman
EMERGENCY TELEPHONE NO. DAY: (414)353-4200 NIGHT: (800)424-9300
INFORMATION TELEPHONE NO. DAY: (414)353-4200 NIGHT: NOT AVAILABLE

SECTION I -- PRODUCT IDENTIFICATION

CONTRACT #GS-10F-51641
MANUFACTURERS CODE IDENTIFICATION: 08609TUA-GD NSN 8010-01-276-3640
PRODUCT CLASS: ALIPHATIC POLYISOCYANATE
TRADE NAME: TAN 686A ZENTHANE, MIL-C-53039A(ME)
HMIS INFORMATION ** HEALTH- 2* FLAMMABILITY- 3
REACTIVITY- 1 PERSONAL PROTECTIVE EQUIPMENT-
HAZARDOUS ITEM PER FED. STD. 313C, PARAGRAPH 3.37 : YES

SECTION II -- HAZARDOUS INGREDIENTS

----- INGREDIENT ----- MATERIAL DESCRIPTION	CAS# / RTECS#	% BY WEIGHT	ACGIH TLV(TWA) PPM	OSHA PEL PPM	OTHER LIMITS RECOMMENDED
METHYL ISOAMYL KETONE SOLVENT	110-12-3 / MP3850000	24.28	50.000	50.000	
PREPOLYMER OF HEXAMETHYLENE DIISOCYANATE	NOT AVAIL. / NOT AVAIL.	30 - 40	NOT EST	NOT EST	
YELLOW IRON OXIDE PIGMENT	51274-00-1 / NO RTECS# FOUND	1.0 - 5.0	NOT EST	NOT EST	NUISANCE DUST
TITANIUM DIOXIDE PIGMENT	13463-67-7 / XR2275000	5 - 10	3.000	3.000	PEL & TLV = 10MG/M3
SILICA PIGMENT	14808-60-7 / VV7330000	20 - 30	0.040	0.040	0.1MG/M3 TLV. & PEL
METHYL ISOBUTYL KETONE SOLVENT ***	108-10-1 / SA9275000	6.26	50.000	50.000	STEL=75PPM
TRIVALENT CHROME PIGMENT ***	7440-47-3 / GB4200000	0.53	0.240	0.240	PEL & TLV = 0.5MG/M3
BUTYL ACETATE SOLVENT	123-86-4 / AF7350000	1.24	150.000	150.000	STEL=200PPM
HEXAMETHYLENE-DIISOCYANATE MONOMER	822-06-0 / MO1740000	0.05	0.005	0.005	
AROMATIC HYDROCARBONS (MIXTURE OF C8'S-C10'S)	64742-95-6 / NO RTECS# FOUND	1.38	NOT EST	NOT EST	100PPM = MFR'S LIMIT

***THESE CHEMICALS ARE SUBJECT TO THE REPORTING REQUIREMENTS OF SECTION 313 OF THE EMERGENCY PLANNING AND COMMUNITY RIGHT-TO-KNOW ACT OF 1986 AND 40 CFR 372.

SECTION III -- PHYSICAL DATA

BOILING RANGE	HIGH 418.0 DF(214C) LOW 232.0 DF(111C)	
VAPOR PRESSURE	15.00	
VAPOR DENSITY	HEAVIER THAN AIR	
EVAPORATION RATE	~~FASTER THAN~~ BUTYL ACETATE	
WEIGHT PER GALLON	10.24	SPECIFIC GRAVITY: 1.23
% VOLATILE BY VOLUME	~~51.36~~	
% VOLATILE BY WEIGHT	34.20	
APPEARANCE-OPAQUE LIQUID		VISCOSITY: 65 - 68 KREBS UNITS
ODOR-SOLVENT ODOR		
PH-NOT APPLICABLE		
WATER SOLUBILITY-REACTS WITH WATER		

SECTION IV -- FIRE AND EXPLOSION HAZARD DATA

FLAMMABILITY CLASSIFICATION OSHA-CLASS IB DOT- FLAMMABLE LIQUID
LOWEST FLASHPOINT T.C.C. 60.0DF (15°C) LOWER EXPLOSION LEVEL (LEL) 0.5
AUTOIGNITION TEMPERATURE: 840F(448C) UPPER EXPLOSIVE LIMIT: 8.2
DECOMPOSITION TEMPERATURE: 400F(204C) MELTING POINT: NOT APPLICABLE
FREEZING TEMPERATURE: NONE MAGNETISM & CORROSION RATE: NOT APPLICABLE
EXTINGUISHING MEDIA: FOAM, DRY CHEMICAL, CO2.
UNUSUAL FIRE AND EXPLOSION HAZARDS: Keep containers tightly closed. Isolate from heat, electrical equipment, sparks and open flame. Closed container may explode when exposed to extreme heat or burst when contaminated with water (CO2 evolved). Do not apply to hot surfaces. Never use welding or cutting torch on or near drum (even empty) because product (even residue) can ignite explosively.
SPECIAL FIREFIGHTING PROCEDURES: Full protective equipment with self-contained breathing apparatus should be worn. During a fire, irritating and highly toxic gases (see Reactivity Data) and smoke are present from the decomposition/combustion products.

SECTION V -- REACTIVITY DATA

NEUTRALIZING AGENT: 3-8% concentrated Ammonia, 2% detergent and 90-95% water; or a solution of Union Carbide's Tergitol TMN-10 (20%) and water (80%).
STABILITY: ( )-UNSTABLE (X)-STABLE
HAZARDOUS POLYMERIZATION ( )-MAY OCCUR (X)-MAY NOT OCCUR
HAZARDOUS DECOMPOSITION PRODUCTS: By fire: CO2, CO, oxides of Nitrogen, traces of Hydrogen Cyanide, Hexamethylene Diisocyanate.
CONDITIONS TO AVOID: Water contamination. INCOMPATIBILITY (MATERIALS TO AVOID): Water, alcohols, glycol ethers, amines.

DOD Hazardous Materials Information System
DoD 6050.5-L
AS OF AUGUST 1992

FSC: 8010
NIIN: 001818079
Manufacturer's CAGE: 98502
Part No. Indicator: A
Part Number/Trade Name: TL 102 (MIL-T-81772A)

General Information

Item Name: THINNER,ALIPHATIC,POLYURETHANE COATING
Manufacturer's Name: SIKKENS AEROSPACE FINISHES DIV. (AKZO COATINGS)
Distributor/Vendor # 1:
Specification Number: MIL-T-81772
Spec Type, Grade, Class: TYPE I
Unit Of Issue: NK
Unit Of Issue Container Qty: N/K
Type Of Container: N/K
Net Unit Weight:

Ingredients/Identity Information

Proprietary: NO
Ingredient: 2-ETHOXYETHYL ACETATE (CELLOSOLVE ACETATE) (EGEEA)
Percent: 39-41
CAS Number: 111-15-9

Proprietary: NO
Ingredient: METHYL ETHYL KETONE (2-BUTANONE) (MEK) (SARA III)
Percent: 29-31
CAS Number: 78-93-3

Proprietary: NO
Ingredient: N-BUTYL ACETATE (SARA III)
Percent: 9-11
CAS Number: 123-86-4

Proprietary: NO
Ingredient: TOLUENE (SARA III)
Percent: 8-12
CAS Number: 108-88-3

Proprietary: NO
Ingredient: XYLENES (O-,M-,P- ISOMERS) (SARA III)
Percent: 6-10
CAS Number: 1330-20-7

Physical/Chemical Characteristics

Appearance And Odor: CLEAR,SOLVENT ODOR.
Boiling Point: 176-321F
Melting Point: N/K (FP N)
Vapor Pressure (MM Hg/70 F): 2-70 MMHG
Vapor Density (Air=1): >1 (AIR=1)
Specific Gravity: 0.89 (H*2O=1)

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